METHOD FOR DETERMINATION OF GASOLINE RANGE ORGANICS

1. Scope and Application

1.1 This method is used o determine the concentration of gasoline range organics in water and soil. This corresponds to an alkane range of C6 - C10 and a boiling point range between approximately 60^{o}C and 170^{o}C. Gasoline or other specific petroleum products may be identified by the use of pattern recognition.

1.2 The practical quantitation limit (PQL) of this method for gasoline range organics is approximately 5 mg/kg for soils and 0.1 mg/L for ground water.

1.3 This method is based on a purge-and-trap, Gas Chromatography (GC) procedure. This method should be used by, or under supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analyst should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.4 With the optional PID detector, this method can be extended for the specific determination of volatile aromatics (BTEX) as specified in SW-846 Method 8020.

2. Summary of Method

2.1 This method provides gas chromatographic conditions for the detection of certain volatile petroleum fractions such as gasoline. Samples are analyzed utilizing purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID) or FID with photoionization detector (PID) in series (PID first in the series). Quantification is based on FID detector response to a gasoline component standard.

2.2 This method is suitable for the analysis of waters, soils or wastes. Water or low level soil samples can be analyzed directly for gasoline range organics by purge-and-trap extraction and gas chromatography. High level soil or waste samples are dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is analyzed by purge-and-trap GC following the normal water method.

3. Definitions

3.1 Gasoline Range Organics (GRO): All chromatographic peaks eluting between 2-methyl pentane and 1,2,4-trimethylbenzene. Quantification is based on a direct comparison of the area within this range to the total area of the 10 components in the gasoline component standard.

3.2 Gasoline Component Standard: A ten component blend of typical gasoline compounds (Table 3). This standard serves as a quantification standard and a retention time window-defining mix for gasoline range organics. It may also be used as the PID calibration standard for the optional determination of BTEX by Method 8020.

3.3 Gasoline Control Standard: A commercial gasoline used by the laboratory as a quality control check. See 7.2.

3.4 Surrogate Control Sample: A reagent water or method blank sample spiked with the surrogate compounds used in the method. The surrogate recovery is used to evaluate method control. See 7.8.

3.5 Laboratory Control Sample: A reagent water or method blank sample spiked with the gasoline control standard. The spike recovery is used to evaluate method control and must be greater than 50%.

3.6 Other terms are as defined in SW-846.

4. Interferences

4.1 High levels of heavier petroleum products, such as diesel fuel, may contain some volatile components producing a response within the retention time range for gasoline. Other organic compounds, including chlorinated solvents, ketones and ethers are measurable. As defined in the method, the GRO results include these compounds.

4.2 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. A trip blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank of reagent water to check for cross contamination. For volatile samples containing high concentrations of water-soluble materials, suspended solids, high boiling compounds or organohalides, it may be necessary to wash the syringe or purging device with a detergent solution, rinse with distilled water, and then dry in an 105oC oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation.

5. Safety Issues

5.1 The toxicity or carcinogenity of each reagent used in this method has not been precisely defined; each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the information of the analyst.

6. Apparatus and Materials

6.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for purge-and-trap sample introduction and all required accessories, including detectors, columns, supplies, recorder, gases and syringes. A data system capable of determining peak areas is required.

6.1.2 Columns

6.1.2.1 Column 1: 105 m x 0.53 mm I.D. Restek RTX 502.2 0.3 micron film thickness, or equivalent.

6.1.2.2 Other columns such as 30 m x 0.53 mm DB-5 may be used - capillary columns are recommended to achieve necessary resolution. At a minimum, the column should resolve 2-methylpentane from the methanol solvent front in a 25 mg/kg LCS standard and should resolve ethylbenzene from m/p-xylenes. Some columns may require subambient cooling to achieve these guidelines.

6.1.3 Detector: Flame ionization detector (FID), or FID in series with a photoionization detector (PID).

6.2 Syringes: 5 mL Luerlock glass hypodermic and a 5 mL gas-tight syringe with shutoff valve.

6.2.1 For purging large sample volumes for low detection limit analysis of aqueous sample for petroleum products, 25 or 50 mL syringes may be used. Subsequently, substitute the appropriate volume in the method wherever 5 mL is stated.

6.3 Volumetric flask: 10 mL, 50 mL, 100 mL, 500 mL and 1000 mL with a ground-glass stopper.

6.4 Microsyringes: 1 uL, 5 uL, 10 uL, 25 uL, 100 uL, 250 uL, 500 uL and 1000 uL.

6.5 Syringe valve: Two-way, with luer ends (three each), if applicable to the purging device.

6.6 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g, and a top-loading balance capable of weighing to the nearest 0.1 g.

6.7 Glass scintillation vials: 20 mL, with screw-caps/crimp caps and Teflon liners or glass culture tubes with a screw-cap and Teflon liner, or equivalent.

6.8 Spatula: Stainless steel.

6.9 Disposable pipets: Pasteur.

6.10 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap and the desorber. Several complete devices are commercially available.

6.10.1 The recommended purging chamber is designed to accept 6 mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1 meets these design criteria. Alternate sample purge devices may be used, provided equivalent performance is demonstrated.

6.10.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105". Starting from the inlet, the trap must be packed with the following adsorbents: 1/2 of 2,6-diphenylene oxide polymer, 1/3 of silica gel and 1/2 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figures 2 and 3). Since only compounds boiling above 35oC are to be analyzed by this method, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Prior to initial use, the trap should be conditioned overnight at 180oC by

backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min. at 180oC with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

6.10.3 The desorber should be capable of rapidly heating the trap to 180oC for desorption. The polymer section of the trap should not be heated higher than 180oC, and the remaining sections should not exceed 220oC during bake-out mode. The desorber design illustrated in Figures 2 and 3 meet these criteria.

6.10.4 Another alternate trap uses 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III (Supelco Cat# 2-0321R). This trap should be desorbed at 240oC and baked to 300oC.

6.10.5 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 4 and 5.

6.10.6 Trap Packing Materials

6.10.6.1 2,6-Diphenylene oxide polymer: 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

6.10.6.2 Methyl silicone packing: OV-1 (3%) on Chromosorb-W, 60.80 mesh or equivalent.

6.10.6.3 Silica gel: 35/60 mesh, Davison, grade 15 or equivalent.

6.10.6.4 Coconut charcoal: Prepare from Barnebey Cheney, CA-580-26 lot #m-2649, by crushing through 26 mesh screen.

7. Reagents

7.1 Reagent Water: Carbon-filtered water purged with helium prior to use.

7.2 Gasoline Control Standards: One reference standard is API PS-6 gasoline, a characterized gasoline used in petroleum research. (Major components in Table 2). Other gasolines of similar composition can be used if they are thoroughly evaluated by the laboratory.

7.3 Gasoline Component Standard: The 10 component quantification standard which also serves as the quantification range (retention time window defining mix) standard. The components and concentration of the 10000 ug/mL stock solution are in Table 3. The standard is prepared by the procedures in 7.4 an 7.5.

7.4 Stock Standards: Prepare a stock standard for the individual gasoline component standards in methanol at approximately 20 mg/mL. The gasoline component standard should be prepared at the concentrations shown in Table 3. Also, a stock gasoline control standard should be prepared.

7.4.1 Place about 8 mL of methanol in a 10 mL tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min. or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.4.2 Using a 25 uL syringe, immediately add appropriate amounts of each gasoline component to the flask. The liquid must fall directly into the alcohol without contacting the

neck of the flask. For the gasoline control standard (using a separate flask), immediately add approximately 125 ul of gasoline to the flask; then reweigh.

7.4.3 Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micrograms per liter (ug/L) for either standard. When compound purity is assayed to be 96% or greater, the volume may be used without correction to calculate he concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.4.4 Transfer the stock standard solution into a Teflon-sealed screw-cap/crimp cap bottle. Store, with minimal headspace, at -10oC to -20oC and protect from light.

7.4.5 Standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.5 Calibration Standards: Calibration standards at a minimum of five concentration levels are prepared in reagent water from the stock standards. One of the concentration levels should be at a concentration near the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. See 9.3.2.

7.6 Internal Standard: Due to potential interferences, the internal standard is not recommended for FID quantification.

7.7 Surrogate Control Standard (SCS): The analyst should monitor both the performance of the analytical system and the effectiveness of the method of dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogate compounds, bromofluorobenzene or trifluorotoluene. Prepare a surrogate spiking solution at 250 ug/mL of the surrogate in methanol. Add 1.0 uL of this surrogate spiking solution directly into the 5 mL syringe with every water sample, low level soil and reference standard analyzed. Surrogate spike solution is added to high level soil samples during the extraction step (see 9.5.1). Other appropriate surrogates may be used (i.e. Isopropyl Toluene).

7.8 Laboratory Control Sample (LCS) Standard: From the stock PS-6 gasoline standard or other appropriate gasoline control standards (Section 7.4), addition of the following amounts yields the indicated concentrations:

10 uL added to 100 uL water: 1 mg/L

0.5 uL added to 5 g soil: 1 mg/kg

8. Sample Collection, Preservation and Handling

8.1 Aqueous samples should be collected in triplicate without agitation and without headspace in contaminant-free glass 40 mL vials with Teflon-lined septa in the caps. The Teflon layer must contact the sample. Sample vials should contain 200 uL of 50% HC1 as a preservative for aromatic analytes. Refrigerate samples at 4oC after collection.

8.2 Soil should be collected in a 4 oz. wide mouth glass jar with a Teflon-lined septa cap. The soil should be disturbed as little as possible and the containers filled as full as possible. Refrigerate all samples at 4^{o}C after collection. Soils for GRO must be analyzed within 14 days of the date collected.

9. Procedure

9.1 Volatile compounds are introduced into the gas chromatograph by purge-and-trap. Purge-and-trap may be used directly on ground water samples. Soils and solids can be analyzed directly or by the methanol extraction procedure, depending upon level of contamination. It is highly recommended that all samples be screened prior to analysis. This screening step may be analysis of a solid sample's methanol extract (diluted), the headspace method (SW-846 Method 3810), or the hexadecane extraction and screening method (SW-846 Method 3820).

9.2 Gas Chromatography conditions (recommended)

9.2.1 Column 1: Set helium column flow to 10 mL/min. Set column temperature to 35^{o}C for 10 min, then 4^{o}C/min to 180^{o}C, then 40^{o}C/min to 220^{o}C and hold for 12.75 min. Conditions may be altered to improve resolution of gasoline range organics.

9.2.2 Other columns-set GC conditions to meet the criteria in 6.1.2.2.

9.3 Calibration

9.3.1 Prepare final solutions containing required concentrations of calibration standards, including surrogate standards, directly in the 5 mL glass syringe. Add the aliquot of calibration solution directly to the reagent water in the glass syringe by inserting the needle through the syringe end. When discharging the contents of the microsyringe, be sure that the end of the syringe needle is well beneath the surface of the reagent water. Attach the 2-way syringe valve to the syringe and then inject the standard into the purge vessel through the two way valve. Proceed with purge-and-trap analysis procedure.

9.3.2 Run the gasoline component standard at a minimum of five concentration levels above the detection limits and covering the expected range of samples or the linear range of the instrument. For the FID quantification of a multicomponent product such as gasoline, the linear range is related to the areas of individual components.

9.3.3 Inject each calibration standard utilizing the purge-and-trap. Tabulate area response for the ten components against mass injected. The results can be used to prepare a calibration curve for the detector. Alternately, the ratio of the amount injected to the response, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the per cent relative standard deviation (%RSD) of the calibration factor is less than 25% over the working range, linearity through the origin can be assumed, and the calibration factor from the midpoint continuing calibration standard can be used in place of a calibration curve.

Calibration Factor = Standard Amount (ng) Purged / Total Area

9.3.4 The working calibration curve or calibration factor must be verified on each working day by the injection of a midpoint continuing calibration standard. If the response for the method standard varies from the predicted response by more than 25% a new calibration curve must be prepared.

Percent Difference = CF1 - CF2 / CF avg. X 100

where:

CF1=Average calibration from the calibration curve.

CF2 = Calibration factor from the midpoint continuing calibration

CF avg.= (CF1+CF2)/2

9.4 Retention Time Window and Pattern Recognition

9.4.1 Before establishing windows, be certain that the GC system is within optimum operating conditions. Make three injections of the gasoline component standard throughout the course of a 72-hour period. Serial injections over less than a 72-hour period result in retention time windows that are too tight.

9.4.2 Calculate the standard deviation of the three absolute retention times for each method standard component.

9.4.2.1 The retention time window for individual peaks is defined as plus or minus three times the standard deviation of the absolute retention time for each component. For multiresponse petroleum products, the analyst may use the retention time window but should primarily rely on pattern recognition.

9.4.2.2 In those cases where the standard deviation for a particular analyte is zero, the laboratory should use +/-0.05 min as a retention time window.

9.4.3 The Laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

9.4.4 Other organic compounds, including chlorinated solvents, ketones and ethers are measurable by this method and will be reported as gasoline range organics.

9.4.5 Note: Although the retention time window definition (2-methylpentane to 1,2,4-trimethylbenzene) introduces a bias, it improves precision and reduces interferences from petroleum products other than gasoline.

9.5 Gas Chromatograph Analysis

9.5.1 Water Samples: Introduce volatile compounds into the gas chromatograph using the purge-and-trap method. Add 1.OuL of surrogate standard to the sample prior to purging.

9.5.1.2 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed t come to ambient temperature, and carefully pour the sample into the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one 40 mL vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has bee analyzed properly. Filling one 5 mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

9.5.1.3 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

9.5.1.4 Dilutions may be made in volumetric flasks (10 mL to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.

9.5.1.5 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this volume of reagent water to the flask.

9.5.1.6 Inject the proper aliquot of samples from the syringe prepared in Paragraph 9.5.1.2 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert and shake three times. Repeat the above procedure for additional dilutions. Alternately the dilutions can be made directly in the glass syringe to avoid further loss of volatiles.

9.5.1.7 Fill a 5 mL syringe with diluted sample as in Paragraph 9.5.1.2.

9.5.1.8 Add 1.0 uL of surrogate spiking solution through the valve bore of the syringe; then close the valve.

9.5.1.9 Attach the syringe-syringe valve assembly to syringe valve on the purging device. Open the syringe valves and inject sample into the purging chamber.

9.5.1.10 Close both valves and purge the sample for 12 min.

9.5.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180^{o}C and backflushing the trap with inert gas between 20 and 60 mL/min for 4 minutes.

9.5.1.12 While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with minimum of two 5 mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover f pollutant compounds into subsequent analyses.

9.5.1.13 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 sec; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180^{o}C. Trap temperatures up to 220^{o}C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7-35 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

9.5.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has a saturated response from a compound, this analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be

decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

9.5.1.15 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

9.5.2 Sediment/soil samples: It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC analysis. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. See 9.1 for recommended screening techniques. Use the screening data to determine whether to use to the low-level method or the methanol extraction technique.

9.5.2.1 Low-level method: This is designed for samples containing low level petroleum products. It is limited to sediment/soil samples and waste that is of a similar consistency. The low-level method is based on purging a soil sample mixed with reagent water containing the surrogate and, if applicable, internal, surrogate and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples.

9.5.2.1.1 Weigh out a 5-g sample into a purge device. Add reagent water to the purge device, cap and agigate. Add 0.5 uL of the surrogate solution to the purge device containing the sample and connect the device to the purge-and-trap system. These steps must be performed in rapid succession to avoid loss of volatiles.

9.5.2.1.2 Purge the sample 12 min. and then proceed as in 9.5.1.11 through 9.5.1.15.

9.5.3 Methanol Extraction for High Level Soil/Sediment: Weigh 10 g (wet weight) of sample into a tared 20 mL vial, using a top-loading balance. Note and record the actual weight to 0.1 gram. Quickly add 10 mL of methanol to the vial. Cap and shake for 2 min. These procedures must be performed rapidly and without interruption to avoid loss of volatile organics.

9.5.3.1 Allow sediment to settle, centrifuge if necessary. Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed. If not analyzed immediately, these extracts must be stored at 4oC in the dark.

9.5.3.2 The GC system should be set up as in Section 9.0. This should be performed prior to the addition of the methanol extract to reagent water.

9.5.3.3 If a screening procedure was followed, use the estimated concentration to determine the appropriate volume of methanol extract. The maximum volume of methanol is 100 uL per 100 mL of reagent water. This is due to the need to separate cleanly the methanol front from the defined retention time window of the gasoline range organics.

9.5.3.4 Calculate the approximate volume of reagent water to be added to the 100 mL volumetric flask and add slightly less than this volume of reagent water to the flask.

9.5.3.5 Inject the proper amount of extract prepared in 9.5.3 into the flask. Dilute the sample to the mark with reagent water. Cap the flask, invert and shake three times.

9.5.3.6 Follow the procedures outlined for a dilution of a water sample as in 9.5.1.7 through 9.5.1.15. Analyze all reagent blanks on the same instrument as that used for the samples. The reagent blank should contain an aliquot of the methanol used to extract the sample.

9.5.4 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with continuing calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

9.5.5 If the responses exceed the linear range of the systems, use a smaller amount of sample.

9.5.6 The calibration factor for the gasoline range organics must not exceed +/-25% when compared to the initial standard of the analysis sequence. When this criteria is exceeded, inspect the GC necessary prior to recalibration and proceeding with sample exceeding QC criteria must be reanalyzed.

9.6 Calculations

9.6.1 The concentration of Gasoline Range Organics in the sample is determined by calculating the absolute weight of analyte purged, from a summation of peak response for all chromatographic peaks eluting between 2-methylpentane and 1,2,4-trimethylbenzene, using the calibration curve or calibration factor determined in 9.3.3. Refer to 9.4 (Retention Time Windows and Pattern Matching). The concentration of Gasoline Range Organics is calculated as follows:

Aqueous or soil samples:

Cs (ng/mL or ng/g) = Ax / Vs or Ms x CF x D

Where:

Cs = Concentration of Gasoline Range Organics.

Ax = Response for the Gasoline Range Organics in the sample, units in area.

CF = Calibration Factor from continuing calibration, units = ng/area.

D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D=1, dimensionless.

Vs = Volume of sample purged, mL.

Ms = Mass of sample purged, g.

10. Quality Control

10.1 The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control. This should include the analysis of QC check samples plus the calculation of average recovery and the standard deviation of the recovery as outlined in Method 8000, Section 8.0.

10.2 After successful calibration (Section 9.3), analyze a Surrogate Control Sample. This standard is also the reagent blank sample and is analyzed with every analytical batch or sequence. The surrogate recovery should be within established limits (Table 4) and the sample should not have Gasoline Range Organics above the practical qualification limit.

10.3 Every batch or 20 samples, duplicate Laboratory Control Samples must be analyzed. The accuracy and precision of the Duplicate standards must be within established limits. (Table 4).

10.4 If any of the criteria is 10.2 and 10.3 are not met, the problem must be corrected before samples are analyzed.

10.5 Calculate sure surrogate standard recovery in each sample. If recoveries are outside established limits, verify calculations, dilutions, and standard solutions. Verify instrument performance.

10.5.1 High recoveries may be due to a coeluting matrix interference-examine the sample chromatography.

10.5.2 Low recoveries may be due to the sample matrix.

10.5.3. Low recoveries may be due to a poor purge (clogged purge tube). If this is suspected, reanalyze the sample while observing the purge tube.

10.6 Field blanks, duplicates and matrix spikes are recommended for specific sampling programs.

11. Method Performance

11.1 The average recovery of gasoline from water samples spiked with 1000ppb was 68% with a Relative Standard Deviation (RSD) of 20 (n=31). The average recovery of gasoline from sediments samples spiked with 1000ppb was 75% with a Relative Standard Deviation (RSD) of 24 (n=24).

12. References

1. USEPA "SW-846 Test Methods for Evaluating Solid Waste", 3rd Edition; Methods 5030, 8000, 8015, and 8030.
2. American Petroleum Institute "Sampling and Analysis of Gasoline Range Organics in Soils", in preparation.
3. "Evaluation of Proposed Analytical Methods to Determine Total Petroleum Hydrocarbons in Soil and Groundwater" prepared by Midwest Research Institute for USEPA Office of Underground Storage Tanks, August 14, 1990.
4. ASTM "Standard Practical For Sampling Waste and Soils For Volatile Organics" Draft #1, 2/16/87.
5. Parr, J.L., G. Walters, and M. Hoffman, "Sampling and Analysis of Soils for Gasoline Range Organics" presented at First Annual West Coast Conference Hydrocarbon Contaminated Soils and Groundwater, 2/21/90.
6. American Petroleum Institute "Laboratory Study on Solubilities of Petroleum Hydrocarbons in Groundwater", August, 1085, API Publ. 4395.

7. "Leaking Underground Fuel Tank (LUFT) Field Manual," State Water Resources Control Board, State of California, Sacramento, California, May, 1988.

8. Fitzgerald, John "Onsite Analytical Screening of Gasoline Contaminated Media Using a Jar Headspace Procedure" in Petroleum Contaminated Soils, Vol. 2, 1989.

9. Senn, R.B., and M.S. Johnson, "Interpretation of Gas Chromatographic Data in Subsurface Hydrocarbon Investigations," Ground Water Monitoring Review, 1987.

10. Hughes, B.M., D.E. McKenzie, C.K. Trang, L.S.R. Minor, "Examples of the Use of an Advanced Mass Spectrometric Data Processing Environment for the Determination of Sources of Wastes" in Fifth Annual Waste Testing and Quality Assurance Symposium; USEPA, July 24-28, 1989.

11. Urban, M.J., J.S. Smith, E.K. Schultz, R.K. Dickson, "Volatile Organic Analysis for a Soil, Sediment or Waste Sample" in Fifth Annual Waste Testing and Quality Assurance Symposium; USEPA, July 24-28, 1989.

12. Siegrist, R.L., and P.D. Jenssen, "Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils", Environmental Science and Technology, Vol. 24, November 9, 1990.

TABLE 1
PURGE AND TRAP OPERATING PARAMETERS

	ANALYSIS METHOD 8020
Purge gas	Nitrogen orHelium
Purge gas flow rate(mL/min)	20-40
Purge time (min)	12.0 +/-0.1
Purge temperature	Ambient
Desorb temperature (oC)	180
Backflush inert gas flow (mL/min)	20-60
Desorb time	4

TABLE 2
MAJOR COMPONENTS OF API PS-6 GASOLINE

Compound	**Percent**	**Weight**
2-Methylbutane	8.72	
m-Xylene		5.66
2,2,4-Trimethylpentane	5.22	
Toluene		4.73
2-Methylbutane	3.93	
n-Butane		3.83
1,2,4-Trimethylbenzene	3.26	
n-Pentane		3.11
2,3,4-Trimethylpentane	2.99	
2,3,4-Trimethylpentane	2.85	
3-methylpentane	2.36	
o-Xylene		2.27
Ethylbenzene	2.00	
Benzene		1.94
p-Xylene		1.72

2,3-Dimethylbutane	1.66	
n-Hexane	1.58	
1-Methyl, 3-ethylbenzene	1.54	
1-Methyl, 4-ethylbenzene	1.54	
3-Methylhexane		1.30

Reference (6)

TABLE 3
GASOLINE COMPONENT STANDARD AND CONCENTRATIONS

Component	**Concentration, (ug/mL)**
2-Methylpentane	1500
2,2,4-Trimethylpentane	1500
Heptane	500
Benzene	500
Toluene	1500
Ethylbenzene	500
m-Xylene	1000
p-Xylene	1000
o-Xylene	1000
1,2,4-Trimethylbenzene	1000
	10000 ug/mL Total

TABLE 4
ACCEPTANCE CRITERIA FOR LABORATORY QUALITY CONTROL CHECKS

Analyte	Spike Concentration	Control Limits	Relative
Laboratory Control Sample	**Water mg/L**	**%Rec**	**%Difference**
Gasoline Range Organics	1.0	50-100	20
Surrogate Control Sample			
Isopropyltoluene	0.05	50-150	